

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 12/31/99	3. REPORT TYPE AND DATES COVERED Final Report 15/SEP/96 to 14/SEP/99	
4. TITLE AND SUBTITLE Core-Level Photoemission Spectroscopy of Metal and Semiconductor Interfaces		5. FUNDING NUMBERS DAAH04-96-1-0425		
6. AUTHOR(S) J.E. Rowe and T.E. Madey				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rutgers University Physics Department Piscataway, NJ 08854-8010		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 36165.3-PH-SR		
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) The goal of the group from NCSU-Rutgers (Jack Rowe's group, in collaboration with Ted Madey) is to use core level photoemission to study interfaces and surfaces of electronic materials and metallic systems. There is also an effort to upgrade this beamline to a Spherical Grating Monochromator (SGM) which is being performed in collaboration with Steve Hulbert of NSLS. Since gate oxides used in current devices have continued to decrease in thickness with corresponding improvements in oxide growth, processing and device properties, we have reinvestigated the issue of the interface of SiO ₂ /Si(111) using the current state-of-the-art methods of gate oxide growth. The Si(2p) core level has a relatively large chemical shift which is nearly ideal for identifying the interface oxide states with SXPS. The bulk Si(2p) binding energy for Si(111) is ~99.3 eV and the bulk Si(2p) oxide value for film thickness ~ 30 Å SiO ₂ is ~103.7 eV. [1] The binding energies of the three interface-shifted peaks are intermediate between these values. These have been assigned by Himpsel et al. [2] as the intermediate oxidation states of Si atoms usually labeled Si ¹⁺ , Si ²⁺ and Si ³⁺ with the bulk Si peak labeled Si ⁰ and the bulk oxide peak labeled Si ⁴⁺ . Beamline U4A has just completed the first phase of a major upgrade. As part of the DOE Facilities Initiative, we are adding spherical gratings and a movable exit slit to the beamline, replacing the toroidal gratings and fixed slits to achieve a spherical toroidal grating monochromator (STGM). More detailed information has become a vital concern in core-electron photoemission studies that were started a few years ago. For example, the reconstruction of Si surfaces results in poorly resolved surface-atom core-electron binding-energy shifts that are not readily determined without reliable information about the instrumental width.				
14. SUBJECT TERMS X-Ray Photoemission, Ultrathin Oxides, Electronics materials Interfaces			15. NUMBER OF PAGES 18	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

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1998 ARO FINAL PROGRESS REPORT

Rutgers University and North Carolina State University

I. General Goals and Objectives.

At Brookhaven National Lab the Rutgers University *et al.* U4A PRT is centered around the use of photoemission spectroscopy to study electronic structure in solids and on surfaces. Two fully equipped surface analysis chambers are used in tandem on the beamline, and the PRT is equipped to make full use of the available synchrotron radiation. The PRT is comprised of groups from Boston University, North Carolina State University/Rutgers University, and the NSLS. Each group has its own independent scientific goals, and the motivation for PRT itself is the use of common synchrotron radiation based spectroscopic techniques. The goal of the Boston University group (Kevin Smith's group) is the study of bulk and surface electronic structure in low dimensional oxide conductors, organic superconductors, and wide band gap semiconductors. The goal of the group from NCSU-Rutgers (Jack Rowe's group, in collaboration with Ted Maday) is to use core level photoemission to study interfaces and surfaces of electronic materials and metallic systems. There is also an effort to upgrade this beamline to a Spherical Grating Monochromator (SGM) which is being performed in collaboration with Steve Hulbert of NSLS.

II. Significant Scientific Results.

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The detailed atomic SiO_2 / Si interface structure and interface state density for ultrathin SiO_2 ($\sim 10\text{-}40 \text{ \AA}$) remains a somewhat controversial topic with some arguing for atomically abrupt (i.e. ~ 1 monolayer, ML) interfaces while others propose a larger transition region of $\sim 10 \text{ \AA}$ thickness. Previous soft x-ray photoelectron spectroscopy (SXPS)

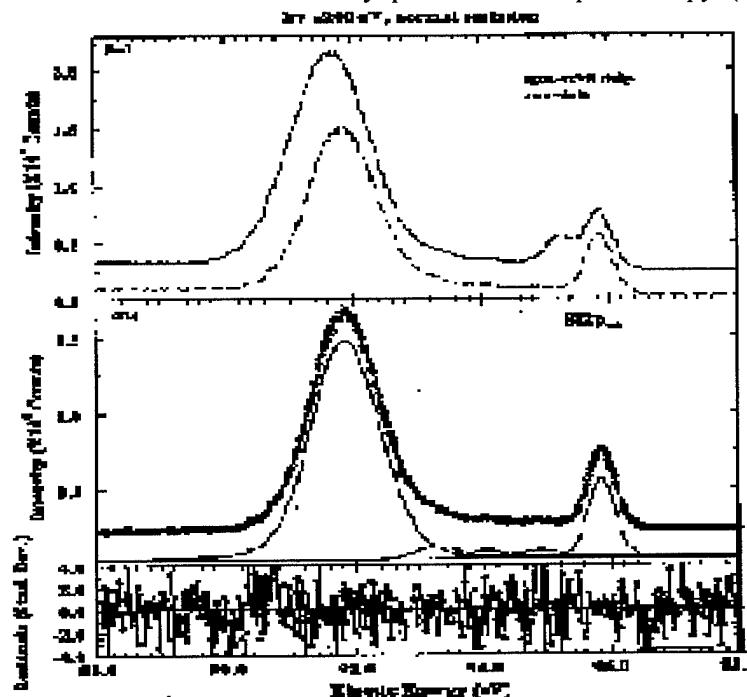


Figure 1 SXPS data for $\text{Si}(100)$ with a 15 \AA SiO_2 layer showing raw data, spin-orbit stripped data, and a non-linear least-squares fit to the stripped data. The lower panel shows the residuals of the fit.

measurements at NSLS by Himpsel *et al.* gave an interface width of $3\text{-}5 \text{ \AA}$ (~ 2 ML) for both (111) and (100) interfaces. A crucial issue that continues to inhibit understanding of spectroscopic measurements is sample preparation at the device-grade level of processing such that interface details can be usefully compared to other measurements. We have used high

resolution SXPS at NSLS to study ultrathin gate oxides grown on Si(111) that achieve these device-quality interface conditions. Since gate oxides used in current devices have continued to decrease in thickness with corresponding improvements in oxide growth, processing and device properties, we have reinvestigated the issue of the interface of $\text{SiO}_2/\text{Si}(111)$ using the current state-of-the-art methods of gate oxide growth. The Si(2p) core level (see Fig.1) has a relatively large chemical shift which is nearly ideal for identifying the interface oxide states with SXPS. The bulk Si(2p) binding energy for Si(111) is ~ 99.3 eV and the bulk Si(2p) oxide value for film thickness ~ 30 Å SiO_2 is ~ 103.7 eV. [1] The binding energies of the three interface-shifted peaks are intermediate between these values. These have been assigned by Himpsel *et al.* [2] as the intermediate oxidation states of Si atoms usually labeled Si^{1+} , Si^{2+} and Si^{3+} with the bulk Si peak labeled Si^0 and the bulk oxide peak labeled Si^{4+} .

Results for surface state density measurements for various samples are shown in Table I. The three columns are for the three interfaces state peaks and are measured in fractional monolayers (ML). The total interface state density is shown in the last column and varies from ~ 1.5 to ~ 2 ML.

Table I. Fitting results summary for interface state densities
(1 ML $\sim 7.8 \times 10^{14}$ cm $^{-2}$ on Si(111)).

sample	Θ_1 (ML)	Θ_2 (ML)	Θ_3 (ML)	$\Sigma\Theta$ (ML)
SiO_2				
as grown (300 °C)	0.87	0.59	0.38	1.84
700 °C	0.92	0.26	0.42	1.60
800 °C	0.82	0.23	0.58	1.63
900 °C	0.79	0.30	0.46	1.56
$\text{SiO}_2 / \text{N}_2^*$				
as grown (300 °C)	0.91	0.48	0.62	2.01
700 °C	0.80	0.41	0.58	1.79
800 °C	0.70	0.42	0.60	1.73
900 °C	0.70	0.42	0.60	1.72

In related experiments on bimetallic catalyst systems, high resolution soft X-ray photoelectron spectroscopy (XPS) is used to study model bimetallic interfaces, i.e., Pt, Pd, Au and Ir films on W (211). The metal film growth and evolution during annealing has been investigated for coverages ranging from 0 to 10 monolayers. It is found that the films grow in a layer-by-layer mode at 300 K. As a function of the overlayer film thickness, several different overlayer 4f_{7/2} photoemission peaks are observed, as shown in Fig. 2 for Pt on W(211),

corresponding to a single monolayer, two interface layer atoms, bulk atoms and surface atoms.

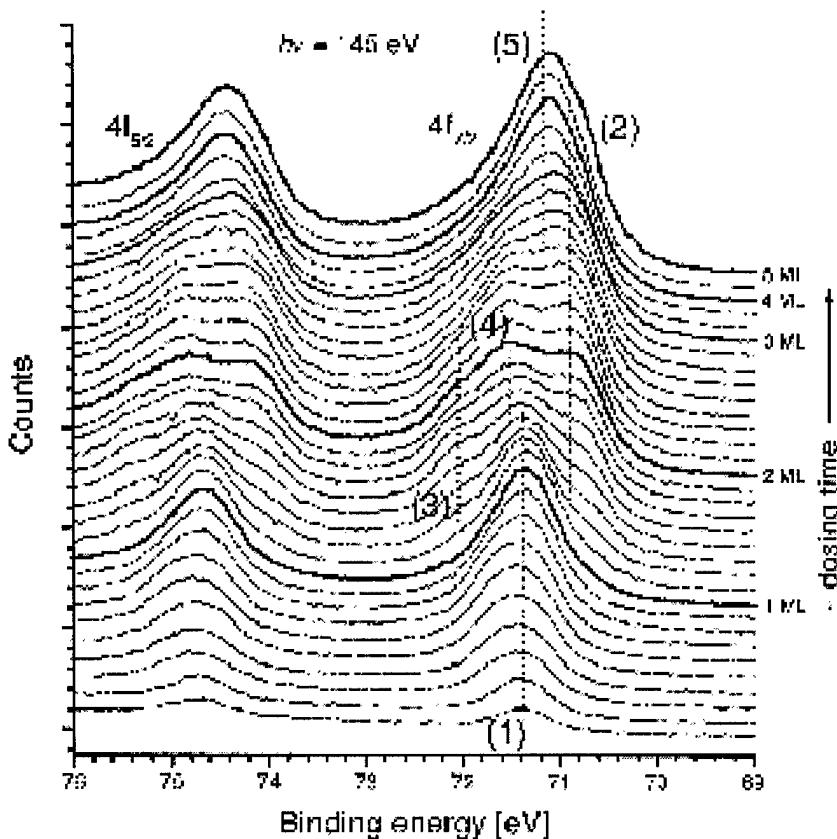


Figure 2 Pt $4f_{7/2}$ and $4f_{5/2}$ SXPS peaks for various coverages on W(211) surfaces. Note that five different Pt peaks are found. Peak (5) is due to bulk Pt.

A single monolayer of each overlayer metal is stable against thermal rearrangement. In contrast, when multilayer films of Pt, Pd, Ir are annealed above 600 K substrate W atoms diffuse into the overlayer to form an alloy - a distinct new W $4f_{7/2}$ peak appears. This peak is shifted ~ 1 eV for Pt and Pd, and about 0.5 eV for Ir, toward higher binding energy as compared with the substrate W peak. In the case of an Au film, no alloying is found. The evolution of the bimetallic systems as a function of coverage and annealing temperature is diagnosed by analysis of intensities and angular dependencies of the substrate and overlayer $4f_{7/2}$ features. Electronic properties are discussed on the basis of the core level peak shifts and shapes and valence band spectra. The data provide detailed information on adhesion, segregation and alloying early d - late d transition metals system. Unusual enhancement of acetylene cyclization reaction over Pd/W(211) model catalyst is found to be related to the formation of a W-Pd surface alloy.

III. Instrumentation and Other Beamline Upgrades.

Beamline U4A has just completed the first phase of a major upgrade. As part of the DOE Facilities Initiative, we are adding spherical gratings and a movable exit slit to the beamline, replacing the toroidal gratings and fixed slits to achieve a spherical toroidal grating monochromator (STGM). A few years ago, modest efforts were made to determine the inherent resolution of the three toroidal gratings that were installed in the late 1980's. In an earlier study the total widths of the Fermi cut-off in the conduction band of Cu(001) were reported to be 230, 140, and 90 meV, for the high, medium, and low energy gratings, G1, G2, and G3 respectively, but no attempt was made to separate the contributions of the TGM itself.

More detailed information has become a vital concern in core-electron photoemission studies that were started a few years ago. For example, the reconstruction of Si surfaces results in poorly resolved surface-atom core-electron binding-energy shifts that are not readily determined without reliable information about the instrumental width. Accurately known core-level line shapes are also required to estimate the disorder broadening associated with adsorbate-covered surfaces. The study of phonon excitations, that accompany the photoemission process similarly requires accurate knowledge of the instrumental contribution to the line width. For bimetallic-overlayer systems, high resolution measurements of surface core level shifts are needed to identify the electronic properties responsible for metal-induced faceting of bcc(111) substrates.

Our objective of the new STGM configuration is to achieve high resolution and high photon throughput. This will be accomplished using the spherical grating monochromator (SGM) design pioneered by the AT&T Bell Labs "Dragon" beamline U4B. This design has now become standard for beamlines in the soft x-ray range. It is less frequently used in the mid-range of 10-200 eV photon energy. However, recent experience on U7 at higher photon energies (200-1000 eV) suggests that the conversion from the modest resolution Toroidal Grating Monochromator (TGM) to the SGM design can be accomplished with a reuse of most beamline components including mirror chambers, grating chamber, scanning mechanism, and slit assemblies. What cannot be reused are the existing gratings (three of them) and one of the two refocusing mirrors. All five of the chambers which are in the beamline (and house these optical elements) were reused in the newly upgraded beamline. In addition, the current exit slit assembly was rebuilt into a movable slit assembly complete with granite block table, constructed at NCSU, using drawings from NSLS. The total cost of the upgrade funded is \$120 K. All other required items have currently been replaced and commissioning of the new STGM configuration is now in progress. The upgrade collaboration was lead by Dr. Steve Hulbert of the NSLS and Prof. Jack Rowe of NCSU. A computer upgrade by the NCSU-Rutgers group has also recently been completed. This computer uses Unix based software written by Gunther Wertheim who is acting as a software consultant to the PRT for monochromator control programs

Rutgers University and North Carolina State University Publications - Copies of papers 3 and 4 are attached.

1. "W(111)-based Bimetallic Systems: Core Level Photoelectron Spectroscopy Studies" H.-S. Tao, T. E. Madey and J. E. Rowe, Surface Science, **407**, L640-L646 (1998).
2. "Ultrathin Metal Films on W(221): Structure, Electronic Properties, and Reactivity" J. J. Kolodziej, K. Pelhos, I. M. Abdelrehim, J. Keister, J. E. Rowe, and T. E. Madey, Progress in Surface Science, **59**, 117-134 (1998).
3. "Structure of Ultrathin $\text{SiO}_2/\text{Si}(111)$ Interfaces Studied by Photoelectron Spectroscopy" J.W. Keister, J. E. Rowe, J.J. Kolodziej, H. Niimi, H.-S. Tao, T. E. Madey, and G. Lucovsky, Journal of Vacuum Science and Technology, **A 17**, 1250-1257 (1999).
4. "Band Offsets for Ultrathin SiO_2 and Si_3N_4 films on $\text{Si}(111)$ and $\text{Si}(100)$ from Photoemission Spectroscopy" J.W. Keister, J. E. Rowe, J.J. Kolodziej, H. Niimi, T. E. Madey, and G. Lucovsky, Journal of Vacuum Science and Technology, **B 17**, 1831-1835 (1999).
5. "Photoelectron Spectroscopy Studies of Adhesion, Segregation and Alloying for Transition Metal-W(211) Bimetallic Systems" J.J. Kolodziej, T. E. Madey, J.W. Keister, and J. E. Rowe, Physical Review B (submitted).